

# The Enthalpy of Solution of SRM 1655 (KCl) in H<sub>2</sub>O

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The value for the enthalpy of solution of SRM 1655 (KCl),  $\Delta H^\circ(500 \text{ H}_2\text{O}, 298.15 \text{ K}) = (235.86 \pm 0.23) \text{ J}\cdot\text{g}^{-1}$  or  $(17.584 \pm 0.017) \text{ kJ}\cdot\text{mol}^{-1}$ , was obtained from measurements in an adiabatic calorimeter, and confirmed by measurements in an isoperibol calorimeter.

Enthalpy of solution measurements are reported in the temperature range 296 K to 358 K, at molalities between 0.005 and 0.18 mol·kg<sup>-1</sup>, for various ranges of particle size up to 1000 μm, and in CO<sub>2</sub>-saturated solutions. Observations were also made relative to the hygroscopicity, removal of occluded H<sub>2</sub>O, and homogeneity of SRM 1655. Between 296 K and 303 K,  $\Delta C_p = -(2.076 \pm 0.087) \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$  or  $-(154.8 \pm 6.4) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  for the reaction of SRM 1655 in 500 H<sub>2</sub>O.

Key words: Adiabatic calorimeter; calorimetry,  $\Delta C_p$ ; endothermic reaction; enthalpy of dilution; enthalpy of solution; KCl; SRM 1655; standard reference material; thermochemistry.

## 1. Introduction

The solution of crystalline potassium chloride in water has for many years been used as an informal reference reaction for endothermic solution calorimetry. In 1974, the Physical Chemistry Division of IUPAC recommended a value,  $(17.55 \pm 0.04) \text{ kJ}\cdot\text{mol}^{-1}$ , for the enthalpy of solution of KCl in 200 H<sub>2</sub>O ( $m=0.2775 \text{ mol}\cdot\text{kg}^{-1}$ ) [1].<sup>1</sup> The National Bureau of Standards (U.S.) Standard Reference Material 999<sup>2</sup> was cited as a source of supply although this material was not used in any of the work on which the recommended value was based. The present work was undertaken to provide a certified value for the enthalpy of solution of the Standard Reference Material (SRM) 1655 based on measurements with SRM 999.

Values for the enthalpy of solution of KCl have long been uncertain. Parker [2] summarized the values reported through 1963 and pointed out that they could be separated into two distinct groups which differed by approximately

150 J·mol<sup>-1</sup> (0.8%). This was probably due to different methods of sample preparation and drying as well as systematic errors in the calorimetry [3]. Gunn [4] showed differences of as much as 35 J·mol<sup>-1</sup> (0.2%) in  $\Delta H_{\text{soln}}$  of samples with different origins and drying procedures. A recent study [5] revealed systematic errors of as much as 0.7 percent in the enthalpy of solution of KBr measured by three high-precision calorimeters. Another recent study [3] showed errors in heat transfer corrections in isoperibol calorimeters due to some calorimetric procedures. These sources of uncertainty can be avoided by the use of a standard reference material of KCl from a single source (such as SRM 1655) if the recommended procedures are followed.

## 2. The KCl Sample

Standard Reference Material 999, potassium chloride (primary chemical), or SRM 1655 was used for all measurements in this work, and KCl refers to the SRM in discussions of the experimental results. A value for the enthalpy of solution of this material has not been certified previously. The existing certification (dated September 6, 1972) is for potassium and chloride content as an analytical standard. The certified assay is  $(52.435 \pm 0.004)$  mass percent potassium and  $(47.551 \pm 0.003)$  mass percent chloride based on the sample dried 4 h at 773 K. Impurities

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<sup>1</sup> Figures in brackets indicate literature references at the end of this paper.

<sup>2</sup> The sample certified for the enthalpy of solution will be designated SRM 1655. It is taken from the same lot as SRM 999, and is available through the Office of Standard Reference Materials, National Bureau of Standards, Washington, D.C. 20234.

detected at greater than  $1 \mu\text{g}\cdot\text{g}^{-1}$  are rubidium ( $27 \mu\text{g}\cdot\text{g}^{-1}$ ) and sodium ( $9 \mu\text{g}\cdot\text{g}^{-1}$ ). The assay after drying is ( $99.98_1 \pm 0.00_7$ ) mass percent based on the potassium determination, and ( $99.99_1 \pm 0.00_6$ ) mass percent based on the chloride determination. The sample was found to be homogeneous within the uncertainty limits reported, and the undried material contains about 0.1 mass percent occluded water. It melts at about 1045 K.

## 2.1. Treatment of Samples for This Work

Ten units (60 g each) were randomly taken from the standard reference material stock of SRM 999 for use in this work and will be referred to as SRM 1655. Ten grams were taken from each of these ten units and mixed; the resulting  $\sim 100\text{-g}$  sample is designated A. Samples B and C were similarly obtained from the same ten units. A portion of sample A was sieved and used in studies of the effects of particle size on volatile matter in the sample and on the enthalpy of solution. Samples B and C were not sieved. They were used in observations of sample homogeneity relative to occluded  $\text{H}_2\text{O}$  and then for enthalpy of solution measurements. Another sample, P, was a unit which had previously been opened and a portion removed for other work; this material was used for some of the exploratory work for this project.

Sample Aa was a 20-g portion of A which was used as received. The remainder of A was sieved through U.S. Standard (bronze) Sieves into the following portions<sup>3</sup>: (1) passed #18 sieve and was retained on #35 sieve, (2) was between #35 and #50 sieves, (2) was between #50 and #100 sieves, and (4) passed #100 sieve. A little less than 40 percent (by volume) of the material was in each of portions (1) and (2), about 20 percent in (3), and less than 1 percent in (4). Only a few particles were retained on the #18 sieve ( $>1000 \mu\text{m}$ ). When sample P was similarly sieved, portion (1) was about 25 percent of the total, portions (2) and (3) were each about 35 percent, and portion (4) about 10 percent. This indicates some inhomogeneity in SRM 1655 with respect to particle size.

The sieved portions of A to be dried at  $\sim 800 \text{ K}$  were designated Ab(1), Ab(2), Ab(3), and Ab(4); those to be dried at  $\sim 525 \text{ K}$  were Ac(1), Ac(2), and Ac(3)—there was not enough of sieve portion (4) to be used in this series. There was only enough of Ab(4) for one calorimetric experiment. The results of heating the various samples will be described in the following section. Table 1 gives a summary of the pretreatment of the various samples used in measurements of enthalpies of solution.

Table 1. Summary of treatment of various samples prior to calorimetric experiments.

Sample Designation	Range of Particle Size $\mu\text{m}$	Drying Temperature K	Sample used in
P(1)	500–1000	---	table 7
P(2)	300–500	---	not used
P(3)	150–300	---	table 7
P(4)	< 150	---	table 7
Aa	unsieved	---	table 5
Ab(1)	500–1000	800	tables 2 and 7
Ab(2)	300–500	800	tables 2 and 7
Ab(3)	150–300	800	tables 2 and 7
Ab(4)	< 150	800	tables 2 and 7
Ac(1)	500–1000	525	tables 2 and 7
Ac(2)	300–500	525	tables 2 and 7
Ac(3)	150–300	525	tables 2 and 7
B	unsieved	800	tables 3,4, and 6
C	unsieved	800	tables 3,4, and 8

At 800 K, samples were dried in a muffle furnace using the potential drop across a chromel-alumel thermocouple to measure the temperature. At 525 K, samples were dried in a laboratory oven using a mercury-in-glass thermometer to measure the temperature. It is estimated that both of these temperature measurements may be uncertain by as much as 1 percent.

## 2.2. Hygroscopicity, Volatile Matter, and Homogeneity

The following observations were made relative to the hygroscopicity of SRM 1655 (KCl):

Sample Aa (20 g as received) was exposed to the laboratory atmosphere ( $\sim 295 \text{ K}$  and  $\sim 40\%$  relative humidity) for nearly 8 h with no detectable change in mass ( $<0.001\%$ ).

Ten grams of Ac(1), which had been heated 5-1/2 h at 525 K in a glass weighing bottle then cooled in a desiccator containing magnesium perchlorate, showed no significant change in mass when exposed to the laboratory atmosphere for 50 min.

A portion of B which had been heated at 800 K in a platinum crucible to remove occluded moisture, cooled, and stored in a desiccator was transferred in air a year later to a capped glass vial for storage in the desiccator. After another 6 months, 16 g was transferred in air to a platinum crucible. Observations for more than 4 h showed no change in mass. This sample was then heated 17 h at 500 K and cooled in a desiccator. A 0.002 percent loss in mass was observed, but exposure to the

<sup>3</sup>The sizes of the sieve openings, which are the present standard designations of these U.S. Standard Sieves, are as follows: #18, 1000  $\mu\text{m}$ ; #35, 500  $\mu\text{m}$ ; #50, 300  $\mu\text{m}$ ; and #100, 150  $\mu\text{m}$ .

atmosphere resulted in no significant ( $<0.001\%$ ) change in mass after more than 2 h. Marinenko [6] found that a sample of SRM 999 exposed to 75 percent relative humidity at room temperature ( $\sim 295$  K) for 8 days showed no significant change in mass; at higher relative humidities adsorption of  $H_2O$  occurred but the water was removed by desiccation over magnesium perchlorate for 24 h.

From these observations, it is apparent that the SRM 1655 (KCl) is not hygroscopic and can be used under the usual laboratory conditions without significant errors due to atmospheric moisture. Therefore, in this work all calorimetric samples were transferred to the sample holder in the laboratory atmosphere.

The removal of occluded moisture from KCl samples is of concern to solution calorimetrists. A review [7] of earlier determinations of the enthalpy of solution of KCl with comments about pretreatment of some of the samples led to the conclusion that values for  $\Delta H_{\text{soln}}$  were low by about 0.2 percent for KCl samples not heated above 600 K. However, no direct measurements were presented in [7] to support this conclusion. Olofsson, et. al., [8] have recommended grinding KCl samples to ensure more complete removal of residual  $H_2O$ .

We have determined the volatile matter in SRM 1655 fractions of various particle sizes by drying at  $\sim 800$  K in platinum crucibles and at  $\sim 525$  K in weighing bottles of borosilicate glass. The results of these measurements are given in table 2 and plotted in figure 1. It can be seen that the amount of volatile matter (assumed to be occluded  $H_2O$ ) increased as the particle size increased; thus the finest material (150 and 300  $\mu\text{m}$ ) contained  $\sim 0.04$  percent less residual moisture than the coarsest material (500 to 1000  $\mu\text{m}$ ). Nearly 0.01 percent more  $H_2O$  was removed by heating 16 h at  $\sim 800$  K than by heating 150 h ( $\sim 6$  days) at  $\sim 525$  K. However, after heating 16 h at 525 K, 0.02 to 0.04 percent residual  $H_2O$  remained in the sample (after only 5 h, 0.03 to 0.06% remained). Heating at lower temperatures would be expected to leave even more residual  $H_2O$  in the sample.

An indication of the homogeneity of the unsieved sample with respect to moisture was obtained from measurement of volatile matter in samples B and C heated in platinum crucibles at  $\sim 800$  K. Measurements were made on 4 portions of each sample and the results are summarized in table 3. It is not surprising that the mean value, 0.066 percent moisture, is close to that determined for Ab(2), which is near the middle of the range of particle sizes (given in table 2). Except for sample 2 of B in table 3, the sample seems to be homogeneous within three times the standard deviation of the mean. The spread of the values is 0.012 percent.

Table 2. Determination of volatile matter in KCl samples of various particle sizes.

(a) Incremental changes in mass after heating at  $\sim 800$  K.

Sample Mass, g	Ab(1) 15.04984	Ab(2) 15.21819	Ab(3) 10.61438	Ab(4) 0.81178
Particle size, $\mu\text{m}$	500 to 1000	300 to 500	150 to 300	$< 150$
mg				
Hours of heating:				
16	-12.78	-9.37	-4.72	-0.31
6	+ 0.20	0.00	+0.18	+0.07
Total loss, %				
	0.085	0.062	0.044	0.034

(b) Incremental changes in mass after heating at  $\sim 525$  K.

Sample Mass, g	Ac(1) 10.11741	Ac(2) 9.99986	Ac(3) 2.56532
Particle size, $\mu\text{m}$	500 to 1000	300 to 500	150 to 300
mg			
Hours of heating:			
5.5	2.53	1.95	0.30
6.5	1.35	0.93	0.15
6	0.88	0.66	0.15
6.5	0.70	0.54	0.19
23	1.17	0.70	0.14
24	0.62	0.36	0.07
66	0.55	0.30	-0.02
44	0.16	0.14	0.07
118	-0.13	-0.22	-0.05
Total loss, %			
	0.078	0.055	0.040

Table 3. Volatile matter in KCl samples B and C dried at  $\sim 800$  K as an indication of  $H_2O$  homogeneity in the unsieved sample. ( $\Delta$  mass and heating time are incremental values.)

Sample No.	1	2	3	4
Mass of B, g	21.71157	27.42042	29.46521	26.98667
Hours of Heating:				
	$\Delta$ mass, mg			
47	-14.72	-16.15	-19.18	-19.05
29	+ 0.15	+ 0.12	+ 0.18	+ 0.18
Total mass loss, %				
	0.067	0.058	0.064	0.070
Mass of C, g	24.21258	29.39481	29.24085	20.38976
Hours of Heating:				
	$\Delta$ mass, mg			
24	-15.50	-20.07	-19.85	-14.53
23	+ 0.15	+ 0.21	+ 0.30	+ 0.20
Total mass loss, %				
	0.063	0.068	0.067	0.070
Mean of 8 = 0.066 %				
Std. dev. of mean = 0.001 <sub>4</sub> %				

### 3. The Adiabatic Calorimeter and Procedures

The measurements of the enthalpy of solution of KCl were made with the platinum-lined adiabatic solution calorimeter described in detail previously [9,10,11]. These references also describe the general procedures followed in this work.

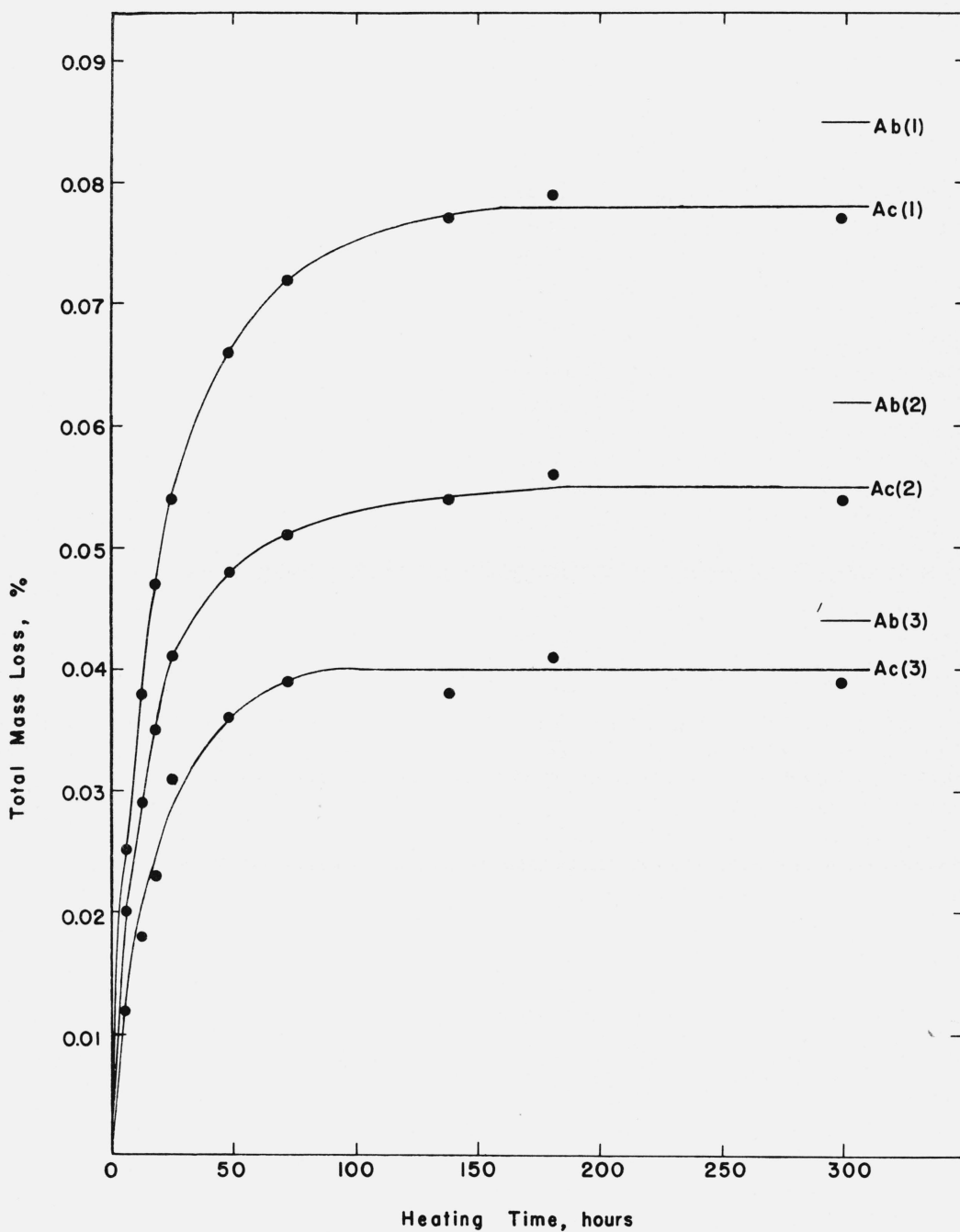


FIGURE 1. Plot showing the incremental loss in mass of SRM 1655 with heating at  $\sim 525$  K for samples with various ranges of particle sizes [Ac(1) is 500 to 1000  $\mu\text{m}$ , Ac(2) is 300 to 500  $\mu\text{m}$ , and Ac(3) is 150 to 300  $\mu\text{m}$ ].

The bars at right for Ab(1), Ab(2), and Ab(3) indicate the total mass lost for comparable samples heated at  $\sim 800$  K for only 16 h.



These calorimetric measurements were done between June and October 1978. The quartz-oscillator temperature-measuring system was calibrated in October 1977 and again in November 1978 by comparison with an NBS-calibrated platinum-resistance thermometer. During this period the calibration remained constant within the uncertainty of the measurements (0.01 K for the absolute temperature and 0.01% for the thermal coefficient in the range 295 K to 330 K). The saturated standard cell and the 0.1- $\Omega$ , 10- $\Omega$ , and 10-k $\Omega$  standard resistors were calibrated by the National Bureau of Standards in December 1977; a long history of calibrations on these electrical standards provides additional confidence in the values used.

The reaction vessel in this adiabatic calorimeter is surrounded by a vacuum ( $P < 0.1$  Pa), the platinum-lined silver vessel has an essentially isothermal polished surface, and the adiabatic shield is automatically controlled to follow the temperature of the reaction vessel; thus, there is negligible heat transfer between the vessel and the surroundings and the system is not subject to the errors in heat leak corrections which may exist in some other calorimeters [3,9].

The "hot or cold" spots due to inadequate stirring, a problem in some calorimeters [3], are relatively unimportant where there is negligible heat transfer between the vessel and the environment. In this calorimeter, the propeller-type stirrer is located immediately below the sample container; this arrangement provides effective stirring. It was confirmed by visual observation in a glass "dummy" reaction vessel that the KCl sample was stirred up into the solution. No crystals were visible after about 3 min at 298 K at the 450 rpm (revolutions per minute) stirring rate used in these experiments except as noted.

The automatic temperature control of the adiabatic shield depends on the addition of electrical energy in response to increases in the calorimeter temperature; if the vessel temperature decreases by as much as 0.1 K, control is temporarily lost and adiabatic conditions are not restored until the vessel temperature increases. During endothermic reactions such as the solution of KCl, it is necessary to add precisely measured electrical energy during the reaction to prevent a decrease in the vessel temperature. Sometimes, at the initiation of very fast endothermic reactions, energy may be absorbed more rapidly than electrical energy can be added. Even if the precaution is taken of beginning the electrical heating 1 or 2 min before starting the reaction, the temperature of the shield may be above that of the vessel for brief periods, and a small correction may be required for heat transfer between the vessel and the shield. Throughout the experiment the temperature difference between the vessel and the adiabatic shield is recorded (detection limit is  $< 0.0001$  K); this time-temperature information is used in calculating the

corrections for departures from adiabatic conditions (see [9]).

The relative molar mass of KCl, 74.5513, and of H<sub>2</sub>O, 18.0152, for this work were obtained from the 1975 Table of Atomic Weights [12]. For energy conversions, 1 thermochemical calorie = 4.184 joules.

#### 4. Enthalpy of Solution Measurements

A certificate value for the enthalpy of solution of SRM 1655 (KCl) was obtained from the results of 53 experiments using the adiabatic solution calorimeter. These experiments will be described and detailed data given in the following subsections (4.1, 4.2, 4.3, and 4.4). Definitions of column headings in the tables are as follows:

Expt. No. is a serial number for the experiments with this calorimeter and indicates the chronological order of the experiments.

The mass of KCl and of H<sub>2</sub>O were corrected to vacuum using buoyancy factors, 1.000455 for KCl and 1.00104 for H<sub>2</sub>O; the density of KCl was taken as 1.98 g·cm<sup>-3</sup> and of H<sub>2</sub>O 1.00 g·cm<sup>-3</sup>. These factors were applicable to the controlled conditions in this laboratory: relative humidity =  $(35 \pm 15)$  percent, temperature =  $(295.6 \pm 0.5)$  K, and pressure =  $(1.00 \pm 0.01)$  MPa or  $(750 \pm 10)$  mm Hg using 0.00118 g·cm<sup>-3</sup> for density of air.

$m$  is the molality of the final solution (moles of KCl/kg of water).

Electrical Energy Equivalents,  $\epsilon_i$  and  $\epsilon_f$ , are given for the system before (initial) and after (final) the solution of KCl. (See [9] for details of the calculations.)

$\Delta T_{\text{obs}}$  is the net temperature change resulting from the absorption of energy during the solution of KCl and the addition of electrical energy during the solution process.

$EE$  is the precisely measured electrical energy added during the endothermic solution of KCl in order to prevent a decrease in the temperature of the reaction vessel.  $EE = EIt$  where  $E$  is the potential drop (in volts) across a 10-k $\Omega$  standard resistor in parallel with the calorimeter heater,  $I$  is the current (in amperes) through the heater obtained from the potential drop across a 0.1- $\Omega$  standard resistor in series with the heater, and  $t$  is the time (in seconds) of electrical heating.  $R = E/I$  is the heater resistance. (See [10] for the calculation details.)

$q_v$  is the vaporization energy for saturating the air space in the sample holder with water vapor. (See [3] for the calculation.) No corrections were made for the condensation of H<sub>2</sub>O in the vapor space above the solutions because they were less than 0.01 J in all experiments.

$q_s$  is a correction for the heat transferred to the vessel when control of the adiabatic shield was temporarily lost

because the initial reaction absorbed energy more rapidly than electrical energy was added. (See [9] for calculations.)

$-Q$  is the energy absorbed during the endothermic reaction and

$$Q = \Delta T_{\text{obs}} \left( \frac{\epsilon_i + \epsilon_f}{2} \right) - EE - q_c - q_s.$$

$T_r$  is the mean of the initial and final temperatures for the reaction period. This is taken as the temperature of reaction.

$\Delta H(m, T_r) = -Q(\text{mass of KCl})^{-1}$ , in  $\text{J}\cdot\text{g}^{-1}$ ; this is multiplied by the molar mass  $\times 10^{-3}$  to obtain  $\text{kJ}\cdot\text{mol}^{-1}$ . This is the enthalpy of solution at the final molality and at the temperature of reaction for the experiment.

$\Delta H^\circ(\infty, 298.15 \text{ K})$  is the standard enthalpy of solution at infinite dilution and at the reference temperature.

$$\Delta H^\circ(\infty, 298.15 \text{ K}) = \Delta H(m, T_r) - \Phi_L - \text{Corr}_{ST}$$

where  $-\Phi_L$  is the enthalpy of dilution obtained from Parker's Table XV A [2].  $\text{Corr}_{ST}$  is the correction to  $T = 298.15 \text{ K}$ , the reference temperature.

$$\text{Corr}_{ST} = \Delta C_p (T_r / \text{K} - 298.15)$$

where  $\Delta C_p = -(154.8 \pm 2.5) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  or  $-(2.076 \pm 0.034) \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$  to be discussed in section 4.1.

The slope of the rating period (RP) time-temperature readings is obtained from the fit of the data to a linear equation by the method of least squares.

$S_{dm}$  is the standard deviation of the mean.

The Reaction Period is the elapsed time between starting the solution reaction (or electrical heating) and starting the rating period following the reaction.

Cal. Unc., the estimated calorimetric uncertainty for an experiment, is calculated from the  $\Delta T_{\text{obs}}$ , the reaction period, and the standard deviation of the rating period slope. For details, see [13].

#### 4.1 Enthalpy of Solution and $\Delta C_p$ of the Reaction

The thermal coefficient for the reaction, of SRM 1655 (KCl) in 500  $\text{H}_2\text{O}$  was determined from 13 measurements of the enthalpy of solution in the temperature range 296 K to 358 K. The data from these experiments are given in tables 4(a and b); the arrangement is in the order of ascending temperature of reaction,  $T_r$ . Sample B was used

in Expts. 1370 and 1371, and sample C in all other experiments (see sec. 2.1); these samples were heated 76 h and 47 h, respectively, at  $\sim 800 \text{ K}$  and had reached constant mass. Loose crystalline samples were used except in Expt. 1371 where the sample was pelleted and the reaction was slower; therefore, electrical energy was added at a lower rate for a longer period (630 s at 12 V; 270 s at 24 V in other experiments). The stirring rate was 550 rpm in Expt. 1395 and 450 rpm in all others.

Table 4b shows information which indicates some of the performance characteristics for this calorimeter. The current,  $I$ , through the calorimeter heater; the potential drop,  $E$ , across the heater; and the resistance,  $R$ , of the heater are given for the three electrical energy measurements (initial calibration, electrical energy added during reaction, and final calibration) in each experiment.

The heater resistance, calculated as the ratio of  $E$  to  $I$ , remained essentially constant,  $(96.70 \pm 0.01)\Omega$ , between 296 K and  $\sim 310 \text{ K}$ . Thereafter, the resistance of the manganin heater decreased with increasing temperature. The values for the heater resistance measured at low voltage are usually more reproducible than those at higher voltages, i.e., Expt. 1371. Experience has shown that above 24 V, the readings of  $I$  and  $E$  are too erratic to give  $R$  values which are reproducible within 0.01 percent. Thus, 24 V across the heater is the practical limit for measurements of high precision.

The slopes of the rating-period time-temperature readings and the standard deviations of the means of these readings are given in table 4b. RP1 precedes the initial calibration, RP2 precedes the reaction with  $EE$  added, RP3 precedes the final calibration, and RP4 finishes the experiment. In general, the slopes decrease as the temperature increases although there are also variations with time caused by changes in bearing surfaces. For example, Expts. 1370, 1371, and 1397 are not in the chronological sequence, and these slopes also depart from the temperature dependent sequence. The slopes are due mainly to the stirring energy which varies somewhat with the viscosity of the solutions. The  $S_{dm}$  values are normally about  $0.5 \mu\text{K}\cdot\text{s}^{-1}$ ; occasional values  $> 1.0 \mu\text{K}\cdot\text{s}^{-1}$  are caused by temporary oscillations of the stirrer (probably started by disturbance of the bearing surface by some minute foreign matter).

The end of the reaction period is more easily determined in this adiabatic calorimeter than in other calorimeters because the slopes of the rating periods are essentially constant throughout the experiment since there is negligible heat exchange with the environment. The reaction is judged to be complete when the difference between successive temperature readings at the 100-s intervals is equal to that preceding the reaction period. A difference of more than

Table 4. Data for measurements of the  $\Delta H_{\text{soln}}$  of SRM 1655 between 296 K and 358 K to determine  $\Delta C_p$  for the reaction.

(a) Enthalpy of solution calculation:

Expt. No.	Mass		m	Elect. Energy Equiv.		$\Delta T_{\text{obs}}$	EE	$-q_v$	$q_s$	$-Q$	$T_r$	$\Delta H(m, T_r)$	
	KCl	H <sub>2</sub> O		Initial	Final							J/g	kJ/mol
	g	g	mol/kg	J/K		K	J	J	J	J	K	J/g	kJ/mol
1386	2.51205	302.404	0.1114	1736.026	1730.249	0.590180	1623.531	0.057	0.084	600.695	296.579	239.125	17.827
1387	2.47630	302.414	.1098	1735.626	1730.527	.592243	1618.508	.058	.057	592.104	296.607	239.109	17.826
1370	2.49038	302.359	.1105	1735.041	1729.432	.597982	1623.003	.062	.076	587.171	298.137	235.776	17.577
1371 <sup>a</sup>	2.48433	302.399	.1102	1733.794	1729.904	.201570	932.944	.064	—	583.791	298.542	234.989	17.519
1388	2.50503	302.379	.1111	1736.028	1730.770	.608846	1630.530	.074	—	575.083	301.340	229.571	17.115
1389	2.51260	302.434	.1114	1736.668	1732.721	.614495	1631.984	.082	.012	565.953	303.170	225.246	16.792
1390	2.50390	302.414	.1111	1737.645	1732.819	.608485	1594.877	.106	—	538.908	308.219	215.228	16.045
1391	2.51265	302.414	.1114	1737.956	1733.448	.637514	1622.178	.138	.024	515.530	313.416	205.174	15.296
1392	2.51497	302.389	.1116	1740.416	1735.642	.664318	1623.464	.221	—	468.639	323.360	186.340	13.892
1393	2.49901	302.379	.1109	1743.052	1738.583	.681402	1607.342	.342	—	420.803	333.164	168.388	12.554
1394	2.49659	302.414	.1107	1746.322	1742.281	.707342	1604.371	.525	—	372.028	343.285	149.015	11.109
1397	2.50515	302.409	.1111	1750.281	1746.142	.737192	1618.058	.751	—	328.539	353.132	131.146	9.777
1395	2.48481	302.389	.1102	1753.306	1749.041	.748091	1611.691	.930	—	300.724	358.874	121.025	9.023

(b) Calorimetric parameters:

Expt. No.	I			E			R			Slope (Sdm)				Reaction Period	Cal. Unc.
	1	2	3	1	2	3	1	2	3	RP1	RP2	RP3	RP4		
	A			V			$\Omega$			$\nu$ K/s				s	%
1386	0.249130	0.249307	0.249357	24.0902	24.1071	24.1122	96.6970	96.6967	96.6973	5.3(0.7)	5.2(0.4)	5.1(0.5)	5.0(0.5)	2300	0.01
1387	.249291	.248836	.248743	24.1056	24.0624	24.0536	96.6966	96.6998	96.7008	5.2(0.5)	4.9(0.7)	4.8(0.6)	4.7(0.8)	2000	.01
1370	.249142	.249326	.249329	24.0916	24.1090	24.1092	96.6982	96.6966	96.6964	4.0(0.5)	3.8(0.4)	3.6(0.5)	3.6(0.6)	2300	.01
<sup>b</sup> 1371	.123807	.123660	.123758	11.9717	11.9578	11.9671	96.6967	96.6984	96.6976	3.7(0.7)	3.7(1.5)	3.8(0.5)	3.7(0.7)	2300	.01
1388	.249060	.249559	.249887	24.0858	24.1317	24.1640	96.7071	96.6973	96.6997	4.4(0.6)	4.4(0.6)	4.3(0.5)	4.3(0.7)	2000	.01
1389	.249285	.249873	.249380	24.1084	24.1617	24.1154	96.7103	96.6962	96.7014	4.4(0.9)	4.4(0.5)	4.4(0.7)	4.6(0.7)	2000	.02
1390	.247822	.246925	.247150	23.9625	23.8769	23.8975	96.6926	96.6969	96.6923	4.1(0.8)	4.2(1.1)	4.2(1.0)	4.3(0.6)	2000	.02
1391	.249319	.249350	.249193	24.1056	24.1080	24.0926	96.6858	96.6834	96.6825	3.9(0.8)	3.9(0.8)	4.1(0.8)	3.9(0.7)	2000	.02
1392	.249370	.249251	.249305	24.1054	24.0939	24.0982	96.6650	96.6653	96.6614	3.2(1.0)	3.2(0.8)	3.3(0.5)	3.3(0.7)	2000	.01
1393	.248636	.248235	.248202	24.0270	23.9878	23.9838	96.6354	96.6335	96.6303	2.7(0.7)	2.7(0.4)	2.8(0.7)	2.7(0.7)	2000	.02
1394	.248715	.247802	.248410	24.0254	23.9388	23.9950	96.5983	96.6048	96.5943	2.0(0.6)	1.9(0.6)	1.9(0.6)	1.7(0.6)	2000	.02
1397	.249525	.248910	.249314	24.0928	24.0338	24.0709	96.5548	96.5562	96.5485	3.4(0.6)	3.2(0.5)	2.6(0.6)	2.8(0.8)	2000	.02
<sup>b</sup> 1395	.248707	.248543	.248996	24.0071	23.9910	24.0328	96.5277	96.5265	96.5190	2.4(0.4)	2.2(0.6)	1.5(1.2)	1.9(1.4)	2000	.05

<sup>a</sup> This sample was pelleted and it dissolved more slowly than the loose crystals; thus, the EE was added for  $\sim 630$  s at lower E and I instead of the 270 s heating in the more rapid reactions.

<sup>b</sup> Stirring rate = 550 rpm; 450 rpm was the stirring rate in the other experiments.

<sup>c</sup> Sample C was used in all experiments except 1370 and 1371 where sample B was used. Both samples were heated at 800 K but were not sieved.

500 s in the length of reaction periods would indicate a prolonged reaction.

The final temperature of the reaction is obtained from an extrapolation of the slope of RP3 back to the time of initiating the reaction. Thus, uncertainty in the slope becomes an uncertainty in the  $\Delta T_{\text{obs}}$ . The estimated calorimetric uncertainty given in table 4b is also influenced by the magnitudes of  $\Delta T_{\text{obs}}$  and of the reaction period although in these experiments the variations in these factors are not significant.

Table 4a gives the information used in calculating the enthalpies of solution at the final concentration and temperature of the reaction. The values for  $\Delta H(m, T_r)$  and the temperature of reaction are plotted in figure 2. When these results were fitted to a quadratic equation by the method of least squares for the purpose of comparison with

the equation given by Olofsson, et al. [8], the following was obtained:

$$\Delta H(500 \text{ H}_2\text{O}, T_r) / \text{J} \cdot \text{mol}^{-1} = 21428$$

$$- 158.0 \{(T_r / \text{K}) - 273.15\} + 0.156 \{(T_r / \text{K}) - 273.15\}^2.$$

The standard deviation of the fit was 25 J·mol<sup>-1</sup> and of the three constants, 48, 2.2, and 0.021, respectively. The slope at 273.15 K is more negative than that of -144.5 J·mol<sup>-1</sup>·K<sup>-1</sup> obtained by Olofsson [8] when they combined their measurements at 450 H<sub>2</sub>O/KCl with those of Vasil'ev and Lobanov. Our values agree at 298 K, but their values show more curvature at higher temperatures.

Most measurements are not made at the high temperatures, and a more practical value for  $\Delta C_p$  was

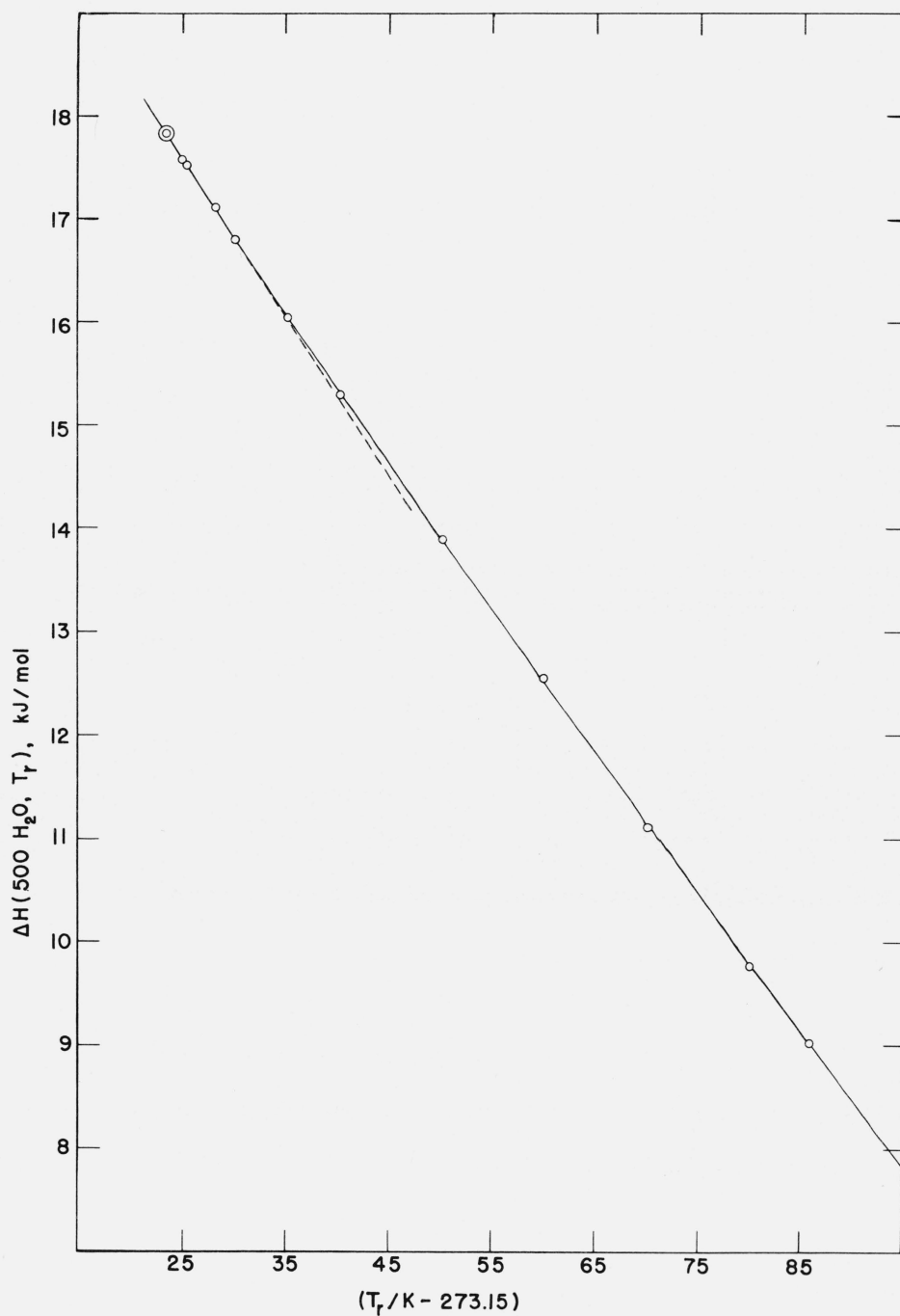


FIGURE 2. Plot showing the relationship of the enthalpy of solution of SRM 1655 in 500 H<sub>2</sub>O to the temperature of reaction.

The slope of the straight line through the 6 points below  $(T_r/K - 273.15) = 28$  corresponds to  $\Delta C_p = (154.8 \pm 2.5) \text{ J} \cdot \text{mol}^{-1}$ .

obtained from fitting our 6 results below 305 K to a linear equation. In the range, 296 to 303 K,  $\Delta C_p = -(154.8 \pm 2.5)$  J·mol<sup>-1</sup>·K<sup>-1</sup> or  $-(2.076 \pm 0.034)$  J·g<sup>-1</sup>·K<sup>-1</sup> for the reaction of SRM 1655 in 500 H<sub>2</sub>O (mean  $m = 0.1107$  mol·kg<sup>-1</sup>). This value is in excellent agreement with that of  $-155$  J·mol<sup>-1</sup>·K<sup>-1</sup> calculated from the equation of Singh, Woolley, McCurdy, and Hepler [14] and using  $51.30$  J·mol<sup>-1</sup>·K<sup>-1</sup> [15] as the heat capacity of KCl(cr).

When the reference temperature, 298.15 K, was subtracted from  $T_r$  for the same 6 experiments, the intercept from the least squares fit was the enthalpy of solution of SRM 1655 in 500 H<sub>2</sub>O at the reference temperature,

$$\begin{aligned}\Delta H^\circ(500 \text{ H}_2\text{O}, 298.15 \text{ K}) &= (235.864 \pm 0.089) \text{ J}\cdot\text{g}^{-1} \\ &= (17.5840 \pm 0.0066) \text{ kJ}\cdot\text{mol}^{-1}.\end{aligned}$$

The uncertainties are the standard deviation of the measured values.

## 4.2. Enthalpy of Dilution

Parker's values [2] for the enthalpy of dilution, or  $-\Phi_L$ , are generally used for corrections to infinite dilution. As an independent check, we have measured the enthalpy of solution of SRM 1655 in 400 H<sub>2</sub>O to 10,000 H<sub>2</sub>O ( $m = 0.14$  to  $0.005$  mol·kg<sup>-1</sup>) although our measurements proved to be unreliable at less than  $0.04$  mol·kg<sup>-1</sup> (1500 H<sub>2</sub>O).

Sample Aa (see sec. 2.1) was used for the 13 experiments in table 5. This sample was neither sieved nor dried, but used as received and corrected for H<sub>2</sub>O as found in other similar samples. Column 2 of table 5 shows that in most of the experiments the calorimetric samples were in the form of loose crystals which reacted quickly when stirred into the solution. In 3 experiments the crystals were tightly packed in the sample holder, and in 3 others, the sample was pelletized with a press and the solution reaction was prolonged 5 to 10 min.

Sample B, dried at  $\sim 800$  K, was used in the 13 experiments in table 6 where two of the calorimetric samples included pellets. Since this material had been dried to constant mass, it was assumed that it contained no residual H<sub>2</sub>O.

The values for the molality and  $\Delta H^\circ(\infty, 298.15 \text{ K})$  from tables 5 and 6 are plotted in figure 3. The radius of the circle surrounding each point is equal to the estimated calorimetric uncertainty. The uncertainties are larger in the dilute region. The circles with shaded areas represent the experiments with the dried sample B, and the open circles are for those with the sample Aa as received. There appears

to be more scatter in the points for the sample as received than for the dried sample indicating that the sample Aa is not homogeneous with respect to moisture and that the corrections for H<sub>2</sub>O are not always adequate. The absence of any apparent slope in the range of molalities from 0.04 to  $0.18$  mol·kg<sup>-1</sup> confirms Parker's values for the dilution corrections. Below  $m = 0.04$  mol·kg<sup>-1</sup> the estimated calorimetric uncertainty was too large for the values obtained to be significant.

Subtracting the value,  $0.343$  kJ·mol<sup>-1</sup> [2], from our enthalpy value for SRM 1655 in 500 H<sub>2</sub>O (see sec. 4.1), we obtain

$$\Delta H^\circ(\infty, 298.15 \text{ K}) = (17.241 \pm 0.018) \text{ kJ}\cdot\text{mol}^{-1}.$$

The uncertainty is the square root of the sum of the squares of the following uncertainties: the experimental standard deviation at the 95 percent confidence level,  $0.017$  kJ·mol<sup>-1</sup>; the uncertainty in the absolute temperature of reaction and the value for  $\Delta C_p$ ,  $0.002$  kJ·mol<sup>-1</sup>; and the uncertainty in the moisture content and in the weights used in determining the mass of KCl,  $0.001$  kJ·mol<sup>-1</sup>.

## 4.3. Effects of Particle Size

In section 2.1 it was shown that SRM 1655 is not homogeneous with respect to particle size. Therefore it was necessary to determine whether the enthalpy of solution is significantly effected by variations in the range of particle sizes in the calorimetric samples.

The results of 11 measurements of the enthalpy of solution of SRM 1655 are given in table 7 where three different samples (P, Ab, and Ac) and four particle size ranges (finest,  $<150$   $\mu\text{m}$ ; medium fine,  $150$  to  $300$   $\mu\text{m}$ ; medium coarse,  $300$  to  $500$   $\mu\text{m}$ ; and coarsest,  $500$  to  $1000$   $\mu\text{m}$ ) were used. These values for the enthalpy of solution are plotted in figure 4 as a function of particle size. The value obtained in Expt. 1368 is quite low and prereaction or an error in the mass of sample is suspected. The high value in Expt. 1362 may be the result of inadequate correction for occluded water in this undried sample. The other measurement with the finest sample was at  $m = 0.036$  mol·kg<sup>-1</sup> where the calorimetric uncertainty is large. Thus, the measurements with the finest material ( $<150$   $\mu\text{m}$ ) are inconclusive. The percentage of the finest particle size in the SRM was relatively small and any error contributed to the total enthalpy of solution would also be small. It is evident that particle size variations in the range,  $150$   $\mu\text{m}$  to  $1000$   $\mu\text{m}$  do not significantly effect the enthalpy of solution, although there may be a trend of slightly increasing enthalpy values as the particle size increases.

Table 5. Data from measurements of enthalpy of solution of sample Aa (SRM1655 as received) corrected for occluded H<sub>2</sub>O at final concentrations about 450 to 5,000 H<sub>2</sub>O/KCl.

Expt. No.	KCl		m	Elect. Energy Equiv.		$\Delta T_{obs}$	EE	$-q_v$	$q_s$	$-Q$	Reaction Period	Cal. Unc.	$T_r$	Corr <sub>ST</sub>	$\Phi_L$	$\Delta H^\circ(\infty, 298.15 \text{ K})$	
	Form	Mass		Initial	Final											J/g	kJ/mol
		g	mol/kg	J/K	J/K	K	J	J	J	J	s	%	K	J/g	J/g	J/g	kJ/mol
c1346	L	2.42493	0.1076	1734.542	1729.761	0.619003	1641.904	0.064	0.027	569.660	2000	0.020	298.3793	0.476	4.56	230.83	17.209
c1347	T	2.58931	.1148	1735.247	1729.523	.594326	1639.901	.061	0.138	610.377	2300	.018	298.1606	0.022	4.59	231.16	17.233
c1348	T	2.65915	.1180	1734.488	1728.476	.584462	1638.631	.059	0.091	626.678	2300	.014	298.1707	0.043	4.62	231.09	17.228
c1349	T	2.57617	.1143	1735.568	1729.432	.598040	1642.416	.061	0.010	606.261	2300	.017	298.1472	-0.006	4.59	230.74	17.202
1350	P	2.56898	.1140	1734.745	1728.827	.177969	910.503	.061	3.82	606.058	2900	.016	298.0088	-0.293	4.60	231.02	17.223
1351	P+L	3.35460	.1488	1734.748	1727.744	.290884	1290.294	.048	1.16	787.814	2900	.015	298.5993	0.934	4.73	231.05	17.225
1352	P	2.56438	.1138	1732.938	1728.848	.478647	1430.362	.063	---	601.812	2600	.016	298.7789	1.307	4.60	231.39	17.250
d1353	L	0.24836	.0110	1730.788	1731.742	-.033354	---	.022	0.250	57.973	1700	.340	297.6627	-1.013	2.31	230.10	17.154
d1354	L	0.51338	.0228	1732.203	1731.009	.285743	613.638	.018	---	118.826	2000	.123	298.6127	0.961	3.00	229.42	17.103
1355	L	0.50947	.0226	1732.617	1731.582	.287684	616.945	.102	---	118.546	2000	.130	298.6154	0.967	3.00	228.72	17.051
1356	L	0.26025	.0115	1733.409	1732.355	-.035126	---	.101	0.233	61.001	1700	.084	297.6403	-1.059	2.35	230.99	17.220
1357	L	1.22094	.0542	1733.838	1730.581	.186598	608.986	.089	0.060	285.730	2000	.026	298.6513	1.042	3.91	231.16	17.233
d1358	L	1.25574	.0557	1734.895	1731.587	.187244	619.693	.053	0.075	295.176	2300	.043	298.3640	0.445	3.94	231.57	17.264

a L means the sample was loosely packed, T means tightly packed, P means the sample was made into a pellet, and P+L was a pellet + loosely packed sample.

b Mass of KCl was corrected for an average of 0.066% H<sub>2</sub>O previously found in unsieved samples (See sec. 2.2).

c The stirring rate in these expts. was 550 rpm and 450 rpm in the other experiments.

d Interchangeable cylinders for the sample holder were used: the smallest (0.7 cm<sup>3</sup>) in Expts. 1353 and 1354, the middle-size (2.0 cm<sup>3</sup>) in Expt. 1358, and the largest (3.0 cm<sup>3</sup>) in all other expts.

Table 6. Data from measurements of enthalpy of solution of sample B(SRM 1655) heated at ~ 800 K). Concentrations of the final solutions are about 12,000 to 300 H<sub>2</sub>O/KCl.

Expt. No.	Mass		m	Elect. Energy Equiv.		$\Delta T_{obs}$	EE	$-q_v$	$q_s$	$-Q$	Reaction Period	Cal. Unc.	$T_r$	Corr <sub>ST</sub>	$\Phi_L$	$\Delta H^\circ(\infty, 298.15\text{ K})$	
	KCl	H <sub>2</sub> O		Initial	Final											J/g	kJ/mol
	g		mol/kg	J/K	J/K	K	J	J	J	J	s	%	K	J/g	J/g	J/g	kJ/mol
1370	2.49038	302.359	0.1105	1735.041	1729.432	0.597982	1623.003	0.062	0.076	587.171	2300	0.013	298.1369	-0.027	4.58	231.17	17.234
a1371	2.48433	302.399	.1102	1733.794	1729.904	.201570	932.944	.064	---	583.791	2300	.012	298.5419	.814	4.58	231.22	17.238
b1372	3.94190	302.389	.1748	1735.515	1727.547	.709211	2154.593	.037	.118	926.653	2600	.014	298.6029	.941	4.76	231.26	17.241
1373	1.99912	302.424	.0887	1734.787	1732.259	.525815	1382.299	.072	.047	470.762	2300	.019	298.1509	.002	4.41	231.08	17.227
1374	1.51189	302.394	.0674	1733.738	1730.289	.599942	1393.507	.082	---	354.317	2300	.022	298.4794	.684	4.13	230.91	17.214
1375	1.25238	302.424	.0555	1734.249	1731.253	.349027	899.750	.085	.002	294.890	2000	.027	298.0757	-.154	3.93	231.38	17.250
1376	0.99700	302.379	.0442	1733.345	1731.409	.094822	398.368	.090	.172	234.182	2000	.024	298.1580	.017	3.67	231.23	17.239
1377	.51597	302.434	.0229	1734.878	1721.866	.158561	395.413	.099	---	120.468	2000	.048	298.2178	.141	3.01	230.61	17.192
1378	.39017	302.454	.0173	1734.312	1733.498	.173079	390.824	.102	---	90.619	2000	.088	298.2162	.138	2.74	229.65	17.121
1379	.29685	302.384	.0132	1733.748	1732.391	-.039485	---	.103	.128	68.455	1700	.087	299.0968	1.967	2.54	230.03	17.149
1380	.20456	302.404	.0091	1733.745	1732.491	-.027381	---	.105	.059	47.409	1700	.131	298.2247	0.155	2.14	229.77	17.130
c1382	.30848	302.404	.0137	1732.091	1732.701	-.041506	---	.021	.159	72.043	1700	.076	298.2567	.222	2.51	231.25	17.240
c1384	.11240	302.404	.0050	1734.231	1732.422	-.015128	---	.025	---	26.197	1700	.197	298.2395	.186	1.67	231.59	17.265

a Pelletted sample.

b Pellet and loose sample.

c Used smallest cylinder (volume = 0.7 cm<sup>3</sup>) in sample holder.



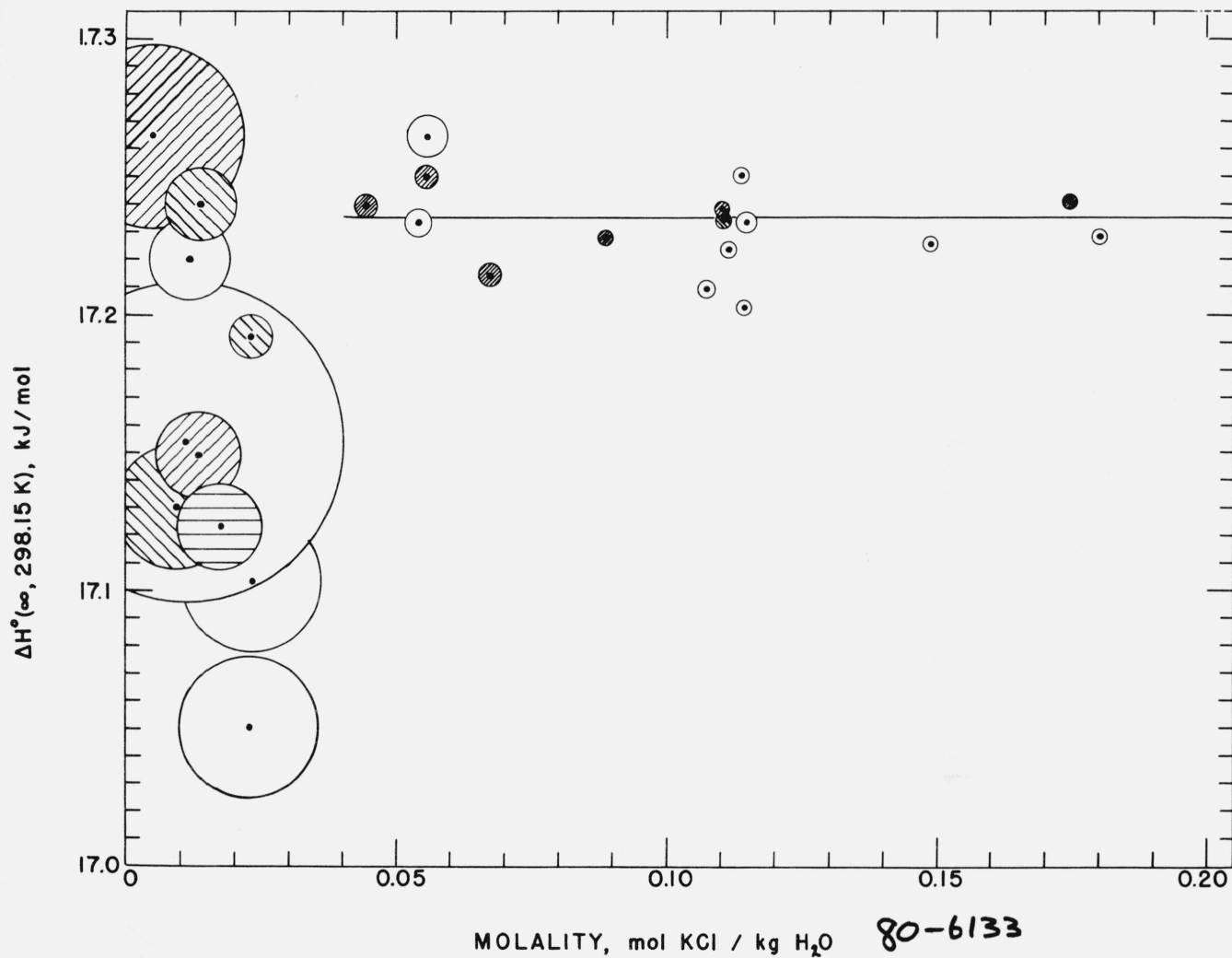


FIGURE 3. Plot of the enthalpy of solution of SRM 1655 at the reference temperature and infinite dilution (using  $\Phi_L$  values from Parker [2]) as a function of molality.

The radius of a circle is equal to the estimated calorimetric uncertainty. Shaded circles are for experiments with a sample dried at 800 K (see table 6). Open circles are for experiments with a sample as received but corrected for occluded  $\text{H}_2\text{O}$  (see table 5). The line shown represents the average of the 7 values of  $\Delta H$  at molalities above  $m=0.04 \text{ mol}\cdot\text{kg}^{-1}$  for the dried sample.



Table 7. Measurements of enthalpy of solution of various samples of SRM 1655 having particle sizes in different ranges up to 1000  $\mu\text{m}$ .

Expt. No.	KCl			H <sub>2</sub> O Mass	Elect. Energy Equiv.		$\Delta T_{\text{obs}}$	EE	$-q_v$	$q_s$	$-Q$	Reaction Period	Cal. Unc.	$T_r$	Corr <sub>ST</sub>	$\Phi_L$	$\Delta H^\circ(\infty, 298.15\text{K})$	
	a Sample	b Size	c Mass		Initial	Final											J/g	kJ/mol
			g	g	J/K		K	J	J	J	J	s	%	K	J/g	J/g	J/g	kJ/mol
1359	P	MF	1.98328	302.419	1733.620	1730.062	0.265809	924.690	0.040	0.252	464.563	2000	0.040	298.6998	1.226	4.40	231.07	17.226
1361	P	C	1.80888	302.354	1734.281	1729.887	.550653	1378.167	.043	---	424.347	2300	.022	298.5742	0.881	4.32	231.15	17.223
1362	P	F	1.99010	302.389	1734.865	1730.408	.525080	1379.257	.038	.014	469.460	2300	.018	298.1578	0.016	4.40	231.51	17.260
1363	Ac	C	2.49788	302.389	1733.883	1729.067	.598515	1625.866	.062	.038	589.528	2300	.015	298.1195	-0.063	4.59	231.36	17.248
1364	Ac	MC	2.52244	302.424	1735.510	1729.496	.598889	1632.495	.062	.060	494.920	2300	.014	298.1361	-0.029	4.59	231.25	17.240
1365	Ac	MF	2.56011	302.379	1735.417	1729.371	.591804	1628.976	.061	.123	603.800	2300	.011	298.1215	-0.059	4.60	231.19	17.236
1366	Ab	F	0.80820	302.399	1734.305	1731.834	.831298	1628.705	.093	---	187.916	2300	.046	299.0510	1.872	3.45	230.93	17.216
1367	Ab	MC	2.49802	302.379	1735.186	1729.846	.595479	1620.700	.062	.082	589.043	2300	.015	298.1321	-0.037	4.59	231.18	17.234
1368	Ab	MF	2.48910	302.389	1735.257	1729.607	.591859	1610.703	.062	.091	585.376	2300	.016	298.1466	-0.007	4.59	230.58	17.190
1369	Ab	C	2.32050	302.389	1735.203	1729.588	.622954	1626.492	.066	.016	547.239	2300	.020	298.1373	-0.026	4.53	231.27	17.242
1385	Ab	MF	2.50015	302.424	1734.592	1729.808	.596594	1622.995	.062	.126	589.638	2000	.011	298.1439	-0.013	4.59	231.24	17.239

<sup>a</sup> See table 1.

<sup>b</sup> C = coarsest, passed #18 and retained on #35 std. sieve (500 to 1000  $\mu\text{m}$ ); MC = medium coarse, passed #35 and retained on #50 std. sieve (300 to 500  $\mu\text{m}$ ); MF = medium fine, passed #50 and retained on #100 std. sieve (150 to 300  $\mu\text{m}$ ); and F = finest, passed #100 std. sieve (< 150  $\mu\text{m}$ ).

<sup>c</sup> Includes the following corrections for occluded H<sub>2</sub>O based on that reported in section 2.2: for P, C = 0.085%, MC = 0.062%; MF = 0.044% and F = 0.034%; for Ac, C and MC = 0.007%; and MF = 0.004%; for Ab, no corrections.

#### 4.4. Effects of Dissolved CO<sub>2</sub>

This adiabatic solution calorimeter and many isoperibol solution calorimeters measure reaction energies at constant pressure and the calorimetric solutions are exposed to the atmosphere, at least through limited vents. It was previously shown [10] that side reactions with dissolved CO<sub>2</sub> apparently occur during the reaction of SRM 724a, tris(hydroxymethyl)aminomethane, in aqueous HCl. The atmosphere normally is composed of only 0.03 to 0.04 mol percent of CO<sub>2</sub>. At equilibrium, very low concentrations of dissolved CO<sub>2</sub> in calorimetric solutions would be expected. These low concentrations of CO<sub>2</sub> can participate in or catalyze side reactions (especially with organic materials) having significant energy effects. Since it would be difficult to determine the amount of CO<sub>2</sub> actually in the calorimetric solutions or the small heat effects if any, measurements of

the enthalpy of solution of SRM 1655 were made under extreme conditions—CO<sub>2</sub>-saturated solutions and essentially CO<sub>2</sub>-free solutions.

In table 8 are the results of 3 measurements of the enthalpy of solution of SRM 1655 in 500 H<sub>2</sub>O using calorimetric solutions saturated with CO<sub>2</sub>, and 2 measurements using essentially CO<sub>2</sub>-free solutions. The procedure and auxiliary equipment were similar to that described previously [10]. The preliminary saturation of the distilled water was done after the assembly of the reaction vessel by bubbling CO<sub>2</sub> gas through the solution for about 30 min before starting temperature measurements. Then the tip of the gas introduction tube was withdrawn to a position several millimeters above the surface of the solution. The flow of CO<sub>2</sub> continued above the solution until after preheating to the desired temperature. The CO<sub>2</sub> flow was discontinued, but the space above the solution was

Table 8. Data from measurements of the enthalpy of solution of sample C (SRM 1655) heated at  $\sim 800\text{K}$  in distilled water saturated with CO<sub>2</sub>, and in CO<sub>2</sub>-free distilled water.

Expt. No.	Mass		Elect. Energy Equiv.		$\Delta T_{\text{obs}}$	EE	$-q_v$	$q_s$	$-Q$	Reaction Period	Cal. Unc.	$T_r$	Corr <sub>ST</sub>	$\Phi_L$	$\Delta H^\circ(\infty, 298.15\text{ K})$	
	KCl	H <sub>2</sub> O	Initial	Final											J/g	kJ/mol
	g	g	J/K		K	J	J	J	J	s	%	K	J/g	J/g	J/g	kJ/mol
CO <sub>2</sub> -saturated solutions:																
1399	2.50177	302.389	1734.011	1728.436	0.591262	1614.806	0.062	0.103	591.240	2000	0.014	297.9894	-0.334	4.59	231.20	17.252
1400	2.51561	302.409	1733.932	1728.312	.590129	1615.242	.063	.058	593.652	2000	.017	298.3274	.369	4.59	231.77	17.278
1403	2.49950	302.414	1734.919	1728.762	.598634	1610.239	.063	.076	589.100	2030	.015	298.3244	.362	4.59	231.46	17.256
															Mean = 17.262	
CO <sub>2</sub> -free solutions:																
1401	2.50281	302.349	1736.321	1730.056	0.583645	1602.180	0.072	0.058	590.599	2000	0.011	298.1144	-0.074	4.59	231.31	17.244
1402	2.49544	302.404	1736.788	1730.817	.586450	1604.540	.062	.027	587.716	2000	.014	298.1166	-.069	4.59	230.86	17.211
															Mean = 17.228	

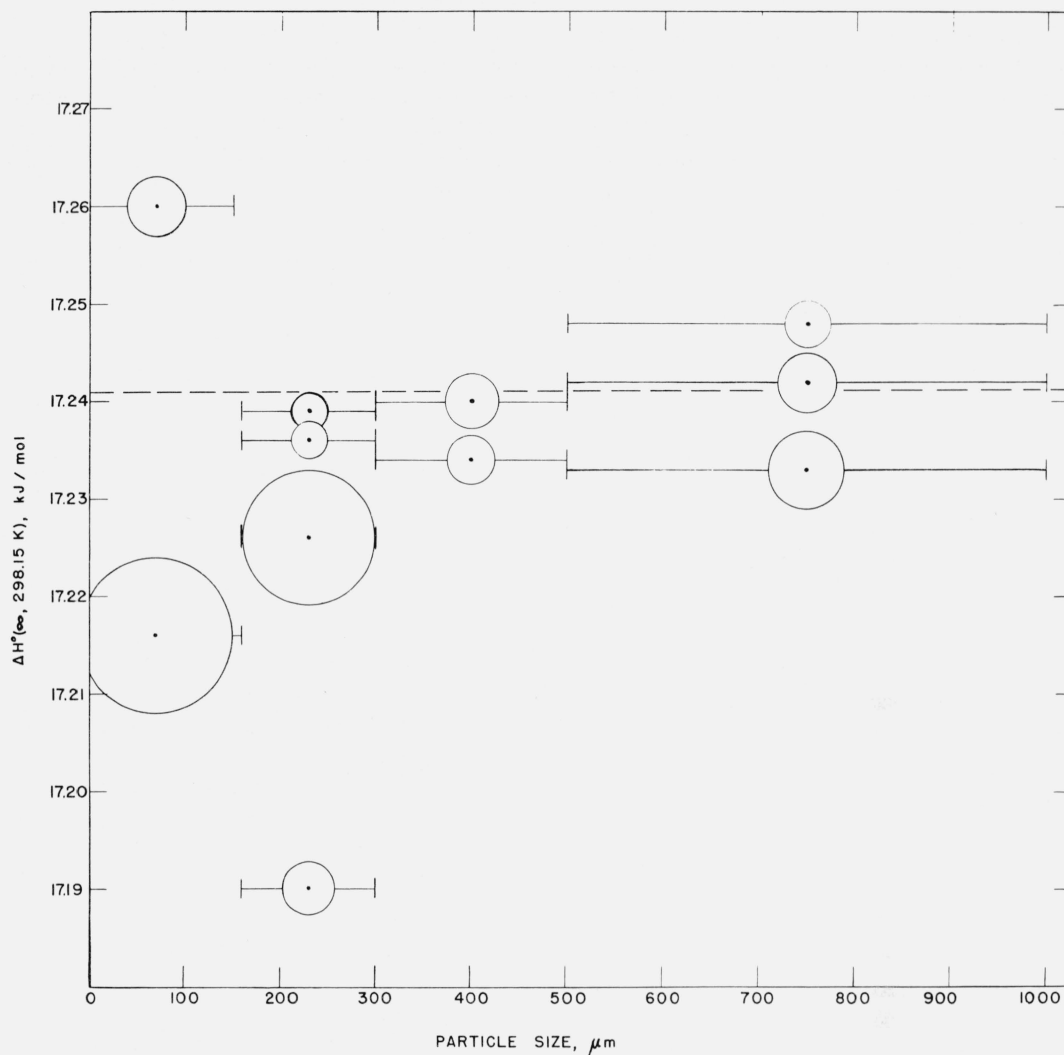


FIGURE 4. Plot of  $\Delta H^\circ(\infty, 298.15 \text{ K})$  for SRM 1655 as a function of sample particle size (as established by sieving).

The radius of a circle is equal to the estimated calorimetric uncertainty for the experiment. The horizontal bars indicate the range of particle sizes in the samples. The dashed line represents the value at infinite dilution calculated in section 4.2. There appears to be no significant effect on the enthalpy of solution attributable to particle size of the sample.

filled with the  $\text{CO}_2$  which diffused slowly from the calorimeter through the limited vent. The calorimetric measurements were completed  $\sim 3.5$  h later. The "CO<sub>2</sub>-free" solutions were freshly boiled distilled H<sub>2</sub>O which was protected during and after cooling by a CO<sub>2</sub>-absorption tube until the calorimetric solution was siphoned off. The solution was exposed to the atmosphere  $\sim 10$  min during weighing; after that, access to the atmosphere was only by diffusion through a hole (2.5 mm in diameter) at the bottom of the vent tube.

The mean values for  $\Delta H^\circ(\infty, 298.15 \text{ K})$  for the two groups of experiments in table 8 differ by only 0.03 kJ·mol<sup>-1</sup> which is almost within the measurement

uncertainty. This small difference could be caused by vaporization effects in the CO<sub>2</sub>-saturated solutions, or differences in the dilution corrections in the presence of CO<sub>2</sub>. At least, the results indicate that errors due to the presence of CO<sub>2</sub> in the calorimetric solutions in equilibrium with the atmosphere, would be negligible.

## 5. Discussion and Summary

Past reluctance to adopt potassium chloride as a standard reference material for endothermic enthalpy of solution measurements, is primarily the result of questions regarding (1) the method of preparation of the KCl sample,

(2) the removal of occluded  $\text{H}_2\text{O}$  in the sample, and (3) disagreement in calorimetric results previously obtained. The first question can be resolved by the use of a large, well-characterized sample from a single source which is readily available. SRM 1655 meets these requirements.

There have been many variations in methods of removing residual moisture in KCl samples ranging from desiccation at room temperature or heating a few hours at relatively low temperatures ( $\sim 400$  K) to actual fusion of the sample at  $>1000$  K. In section 2.2 we have shown that nearly 0.01 percent of occluded  $\text{H}_2\text{O}$  remained in coarse SRM 1655 samples after heating 4 to 5 days at  $\sim 525$  K. Olofsson [8] stressed the importance of using finely ground samples. Our observations confirmed this by the fact that when an SRM 1655 sample of particle size  $<150$   $\mu\text{m}$  was heated at  $\sim 800$  K, residual moisture was  $\sim 0.04$  percent as compared to  $>0.08$  percent for a sample of particle sizes in the range  $500$   $\mu\text{m}$  to  $1000$   $\mu\text{m}$ . Grinding the SRM is not recommended because of the risk of contamination; heating at  $800$  K is recommended (this is safely below the fusion temperature where alterations of the crystal structure might occur.)

The disagreement in results obtained in previous measurements of the enthalpy of solution of KCl were probably due not only to different methods of sample preparation and removal of residual  $\text{H}_2\text{O}$ , but also to errors in calorimetry as discussed in the preceding paper [3]. In that work it was shown that when the recommended procedures were used, the value for the enthalpy of solution of SRM 1655 measured in the isoperibol calorimeter agreed within  $\sim 0.01$   $\text{kJ}\cdot\text{mol}^{-1}$  (0.05%) with that in the adiabatic calorimeter.

In this work the enthalpy of solution of SRM 1655 in  $500$   $\text{H}_2\text{O}$  ( $m=0.111$   $\text{mol}\cdot\text{kg}^{-1}$ ) was measured as

$$\begin{aligned}\Delta H^\circ(500 \text{ H}_2\text{O}, 298.15 \text{ K}) &= (235.86 \pm 0.23) \text{ J}\cdot\text{g}^{-1} \\ &= (17.584 \pm 0.017) \text{ kJ}\cdot\text{mol}^{-1}.\end{aligned}$$

The assigned uncertainty is the square root of the sum of the squares of the following uncertainties: the standard deviation of the experimental values at the 95 percent confidence level, 0.097 percent; uncertainty in the absolute temperature of reaction and  $\Delta C_p$ , 0.011 percent; and uncertainty in the moisture content and in the weights used to determine the mass of KCl, 0.006 percent. The  $\Delta C_p$  measured for this dissolution is  $-(2.076 \pm 0.087) \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$  or  $-(154.8 \pm 6.4) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  in the range,  $296$  K to  $303$  K. The uncertainties are at the 95 percent confidence level.

In the preceding paper, results are reported for measurements of the enthalpy of solution of SRM 1655 in an isoperibol calorimeter [3]. The average from 5 experiments at the adequate stirring rate and  $m=0.094$   $\text{mol}\cdot\text{kg}^{-1}$  was  $\Delta H^\circ(298.15\text{K})=17.566$   $\text{kJ}\cdot\text{mol}^{-1}$ . When corrected to  $m=0.111$   $\text{mol}\cdot\text{kg}^{-1}$ ,

$$\Delta H^\circ(500 \text{ H}_2\text{O}, 298.15 \text{ K}) = (17.578 \pm 0.075) \text{ kJ}\cdot\text{mol}^{-1}.$$

The experimental uncertainty given is at the 95 percent confidence level. This is in excellent agreement with the value obtained with the adiabatic calorimeter.

The value recommended by the Physical Chemistry Division of IUPAC [1] for the enthalpy of solution of KCl in  $200$   $\text{H}_2\text{O}$ ,  $(17.55 \pm 0.04) \text{ kJ}\cdot\text{mol}^{-1}$ , is based primarily on the work of Olofsson, et al., [8] using another KCl sample. This value also applies at  $500$   $\text{H}_2\text{O}$  because  $\Phi_L$  is essentially the same at these concentrations. Parker's "best" value at infinite dilution selected from measurements reported prior to 1963 [2] was  $(17.22 \pm 0.04) \text{ kJ}\cdot\text{mol}^{-1}$ ; this corresponds to  $17.56 \text{ kJ}\cdot\text{mol}^{-1}$  at  $500$   $\text{H}_2\text{O}$ , in remarkably good agreement with the values obtained by Olofsson [8] and this work where great care was taken to achieve high precision and accuracy. Thus it is reasonable to assume that the enthalpy of solution of SRM 1655 is also that for pure KCl.

The endothermic solution of SRM (KCl) in water now appears to be a good standard reference reaction for the following reasons:

- (1) The solute and solvent are of high purity and readily available.
- (2) The reaction is rapid and complete and values for the temperature coefficient of the reaction enthalpy and enthalpies of dilution are well-defined.
- (3) The solute is nonvolatile and nonreactive with components of the atmosphere.
- (4) The removal of residual  $\text{H}_2\text{O}$  from the solute has been studied so that the final purification of the sample by the user may be easily and reproducibly accomplished.
- (5) Values for the enthalpy of solution of SRM 1655 have been determined from measurements in both an adiabatic and an isoperibol calorimeter. These values agree with each other as well as with other determinations where careful attention was given to sample purity and accuracy of the measurements.

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